Laser Absorption Measurements of CO at Elevated Pressures behind Reflected Shock Waves

A. Camou, J.E. Vivanco, D.M. Cusano, and E.L. Petersen

1 Introduction

Laser absorption spectroscopy has played a major role in combustion measurements and temperature sensing. Laser spectroscopy techniques offer non-intrusive measurements that can predict gas composition in combustion systems such as IC engines and power plants, as well as in the atmosphere. A model for sensitive measurements of carbon monoxide has been developed using direct absorption spectroscopy near 4.5 μm. An accurate prediction of CO concentration is important due to its toxicity as well as its direct relation to combustion inefficiency. The model was used to predict the absorption time-history of a CO/Ar mixture in a shock tube at Texas A&M University. This paper presents the details of the laser absorption diagnostic and provides some results for CO measurements at elevated temperatures and pressures using a shock tube.

2 Absorption Spectroscopy and Line Selection

Direct absorption spectroscopy (DAS) is a technique that relates the attenuation of laser intensity along a fixed path to the absorbance of a gas species. A collimated laser beam with an intensity I_0 passes through a gas sample with a fixed length L. The laser energy is absorbed when the laser frequency ν [cm^{-1}] is resonant with the frequency of a transition line of the absorbing species within the gas mixture. The laser intensity attenuation is related to the absorbance of species *i* by the Beer-Lambert Bouger law:

A. Camou · J.E. Vivanco · E.L. Petersen
Department of Mechanical Engineering,
Texas A&M University, College Station, TX 77843, USA

D.M. Cusano
Parametric Solutions, Inc., Jupiter, FL 33477, USA

R. Bonazza and D. Ranjan (eds.), *29th International Symposium on Shock Waves 1*,
DOI: 10.1007/978-3-319-16835-7_33

$$\left(\frac{I_t}{I_0}\right)_\nu = exp(-k_\nu L) \tag{1}$$

where I_t is the transmitted intensity after the beam passes through the gas sample, and the absorption coefficient is defined as:

$$k_\nu = SPx_i\phi_\nu \tag{2}$$

where S [cm^{-2} atm^{-1}] is the absorption line-strength of the specific species transition, P [atm] is the total pressure, x_i the mole fraction of the absorbing species i, and ϕ_ν [cm] is the Voigt line-shape function. The absorbance is defined as the dimensionless product:

$$\alpha_\nu = ln\left(\frac{I_t}{I_0}\right) SPx_i\phi_\nu L \tag{3}$$

The Voigt line-shape function is a convolution of both Doppler and collisional broadening characterized by the Gaussian and Lorentz profiles, respectively. The broadening parameters as well as the absorption line-strength for CO are computed based on the HITRAN database.

Extensive studies of CO detection in the first and second overtone band have been carried out using different laser absorption techniques. Mihalcea *et al.* [1] employed a fiber-optic diode laser system to measure combustion emission species such as CO, CO_2, and NO in the second overtone band ($\Delta\nu = 3$) near 1.55 μm. Chao *et al.* [2] employed a tunable diode laser absorption spectroscopy (TDLS) sensor as well as a wavelength modulation spectroscopy (WMS) sensor for CO detection in the first overtone band ($\Delta\nu = 2$) near 2.3 μm. Lin *et al.* [3] also investigated the CO detection near 2.3 μm by coupling optical emission spectroscopy (OES) and TDLS techniques. However, the absorption line-strengths of dominant combustion products H_2O and CO_2 were comparable to CO line-strengths near 1.55 and 2.3 μm which limited the CO detection limit.

The fundamental band ($\Delta\nu = 1$) near 4.5 μm was proven to have significantly higher CO absorption line-strengths compared to the first and second overtone bands near 2.3 and 1.55 μm, respectively. In addition to the higher line-strengths, the absorption from dominant interfering species such as H_2O and CO_2 were proven to be minimal near 4.5 μm [4]. CO detection in the fundamental band has been investigated by Barron Jimenez *et al.* [5] using a difference-frequency-mixing based diode laser sensor. However, the low mid-IR power of the diode laser of less than 1 μW limited the sensitivity and signal-to-noise ratio for CO detection. Ren *et al.* [4] employed a distributed feedback quantum cascade laser (DFB-QCL) to access the fundamental band of CO near 4.5 μm. The DFB-QC lasers provide a higher power (mW) that result in higher-sensitivity measurements.

The fundamental band of CO near 4.5 μm was selected for this paper due to its higher CO absorption line-strength compared to interfering species H_2O and CO_2. This band allows for lower CO concentration detection limits. The air and self broadening parameters as well as absorption line-strengths of CO were obtained using the HITRAN 2004 database.

3 Experiment

All spectroscopic measurements were performed in a stainless steel shock tube located at Texas A&M University with an internal diameter of 15.24 cm. More details can be found in Aul *et al.* [6]. A schematic of the shock tube endwall region and optical experimental setup is shown in Fig. 1. The incident shock wave propagates through the shock tube, heating the mixture temperature and pressure from (T_1,P_1) to (T_2,P_2) and eventually reflects from the endwall of the shock tube. The mixture is then raised to (T_5,P_5) after the reflected shock wave propagates through.

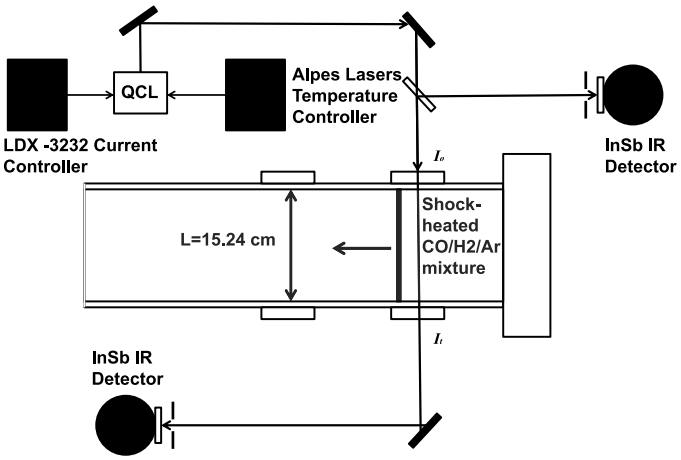

Fig. 1 Experimental setup of absorption measurements for CO near 4.5 μm in the shock tube at Texas A&M University (only the endwall region is shown).

A DFB QC laser from Alpes Lasers was used to access the fundamental band of CO near 4.5 μm. The QCL is housed in a sealed package (Alpes HHL housing) that includes collimation optics and is controlled by a LDX-3232 current controller and a temperature controller provided by Alpes Lasers. The current and temperature are tuned to access the R(12) CO branch. The line was validated by comparing the calibration data provided by Alpes Laser with CO/Air spectroscopic measurements conducted in the shock tube. Two InSb IR detectors from Teledyne Judson Technologies were used for the optical detection measurements. A series of irises and

bandpass filters was used to block out interference emission and any unwanted light from other wavelengths. A mixture of 0.1% CO, 5% H_2, and 94.9% Ar was utilized for the results presented herein. Hydrogen was added to the mixture to minimize the vibrational relaxation time of CO behind the reflected shock wave.

4 Results and Discussion

Figure 2 and Fig. 3 illustrate two time-history cases of CO absorption as the shock wave propagates through the mixture. A P_5 behind the reflected shock wave of 1.62 atm is plotted in Fig. 2, and a P_5 of 10.8 atm is plotted in Fig. 3. Figure 4 illustrates the simulated spectra of CO near 4.5 μm. The simulation is zoomed into the CO transition ($v" = 0$, R(12)). Ar-broadening parameters were determined by Ren *et al.* [4] for a temperature range of 1100 - 2000 K.

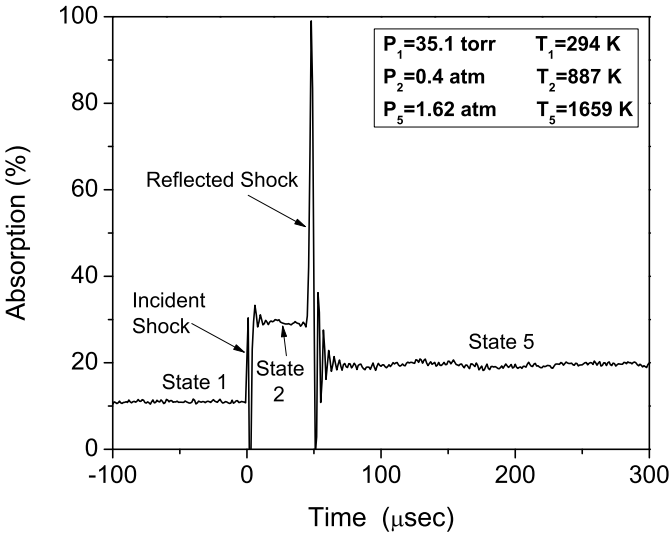

Fig. 2 Fixed-wavelength CO absorption time history in the shock tube at lower pressure with 0.1% CO, 5% H_2, 94.9% Ar; pressure and temperature behind reflected shock wave were 1659 K and 1.62 atm, respectively.

The simulation (shown in Fig. 4 for 10.8 atm) over predicts the absorption at P_2 but accurately predicts it at P_5 at the simulated absorption peak. The noise level at P_5 is greater due to the higher pressure conditions, which introduce turbulence and beam steering effects. The schlieren spikes show generate a high signal which may be due to the small InSb detector active diameter of 1 mm. Additional spectroscopic measurements need to be conducted to extend the Ar-broadening parameters on CO to a larger temperature range to better predict the absorption of CO.

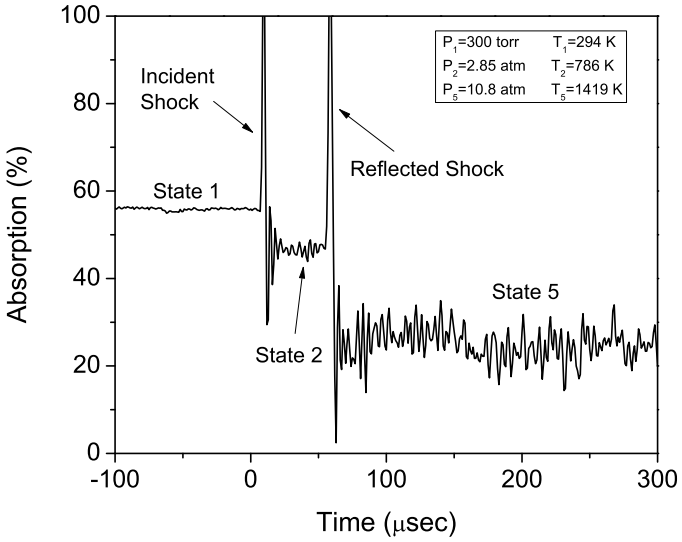

Fig. 3 Fixed-wavelength CO absorption time history in the shock tube at higher pressure with 0.1% CO, 5% H_2, 94.9% Ar; pressure and temperature behind reflected shock wave were 1419 K and 10.8 atm, respectively.

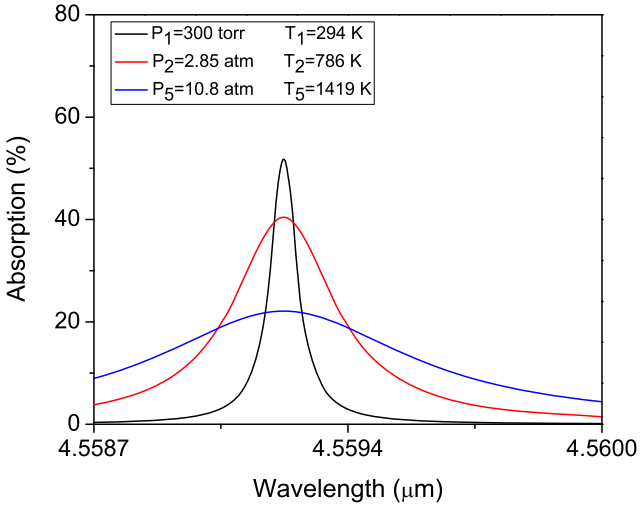

Fig. 4 Simulated absorption spectra for 0.1% CO, 5% H_2, 94.9% Ar, corresponding to the higher-pressure conditions in Fig. 3.

5 Conclusion

A quantum-cascade laser system was employed in the athors' laboratory at Texas A&M University to measure the concentration of CO at a wavelength near 4.5 μm.

Shock-tube experiments were performed using mixtures of 0.1% CO highly diluted in argon, with 5% H_2 by volume added to each mixture to speed up the vibrational relaxation of the CO; tests near 1 atm and 10 atm behind reflected shock waves were performed to demonstrate the QCL absorption setup and relevant spectroscopic calculations at elevated temperatures (1400 - 1700 K).

References

1. Mihalcea, R.M., Baer, D.S., Hanson, R.K.: A diode-laser absorption sensor system for combustion emission measurements. Meas. Sci. Technol. 9, 327–338 (1998)
2. Chao, X., Jeffries, J.B., Hanson, R.K.: Absorption sensor for CO in combustion gases using 2. 3 μm tunable diode lasers. Meas. Sci. Technol. 20, 115201 (2009)
3. Lin, X., Yu, X.L., Li, F., Zhang, S.H., Xin, J.G., Chang, X.Y.: CO concentration and temperature measurements in a shock tube for Martian mixtures by coupling OES and TDLAS. App. Phys. B 110, 401–409 (2013)
4. Ren, W., Farooq, A., Davidson, D.F., Hanson, R.K.: CO concentration and temperature sensor for combustion gases using quantum-cascade laser absorption near 4. 7 μm. App. Phys. B 107, 849–860 (2012)
5. Jimenez, R.B., Caton, J.A., Anderson, T.N., Lucht, R.P., Walther, T., Roy, S., Brown, M.S., Gord, J.R.: Application of a difference-frequency-mixing based diode-laser for carbon monoxide detection in the 4.4-4.8 μm spectral region. App. Phys. B 85, 185–197 (2006)
6. Aul, C.J., Metcalfe, W.K., Burke, S.M., Curran, H.J., Petersen, E.L.: Ignition and kinetic modeling of methane and ethane fuel blends with oxygen: a design of experiments approach. Combust. Flame (2013)